Adsorption, formation, and transport of molecular water on lunar regolith

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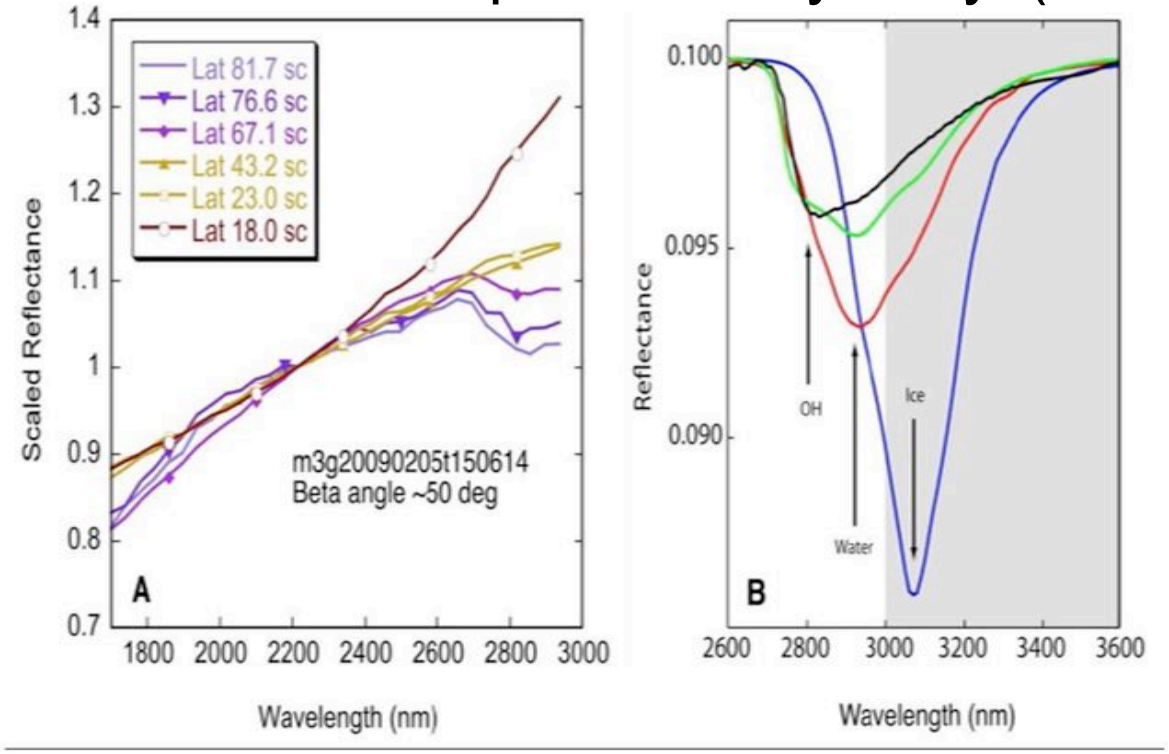
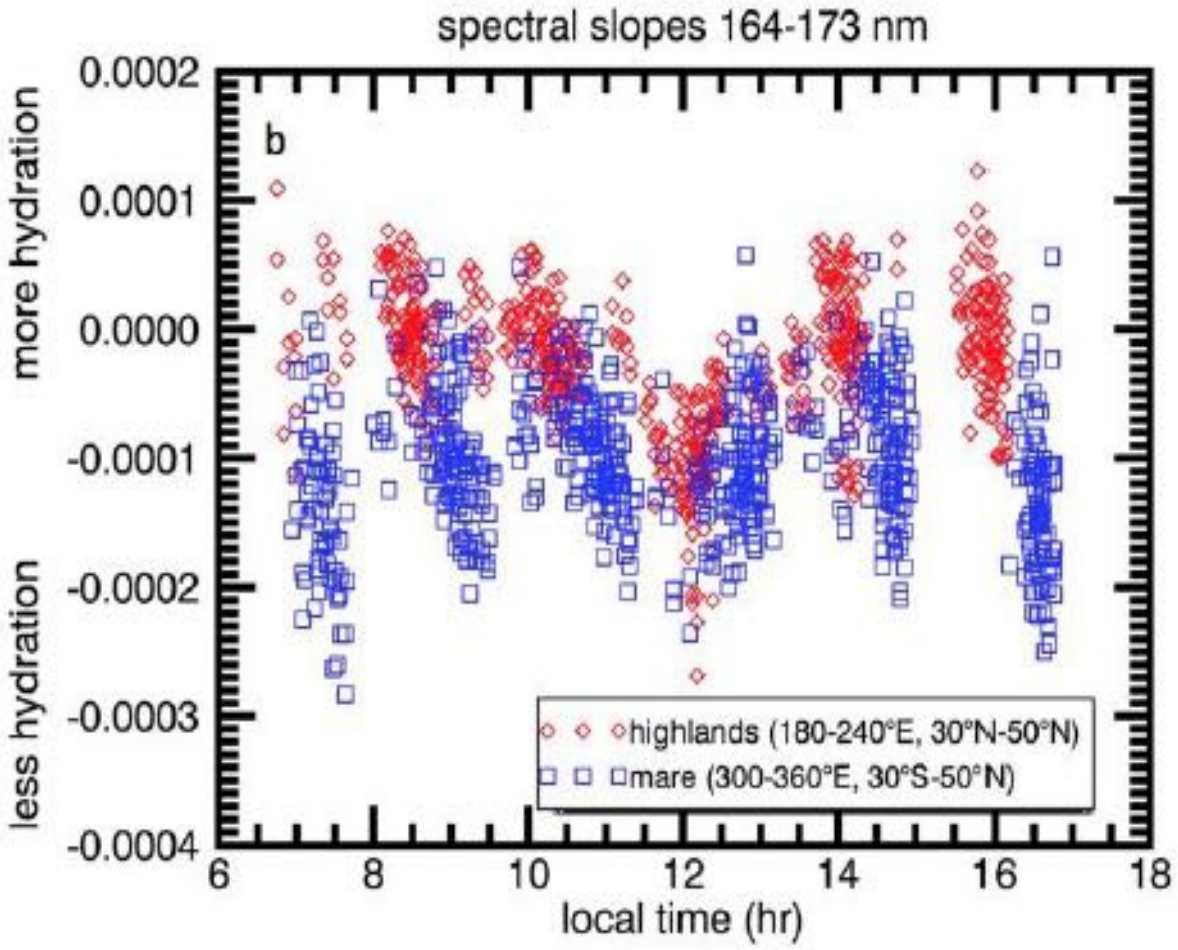
Water on the Moon

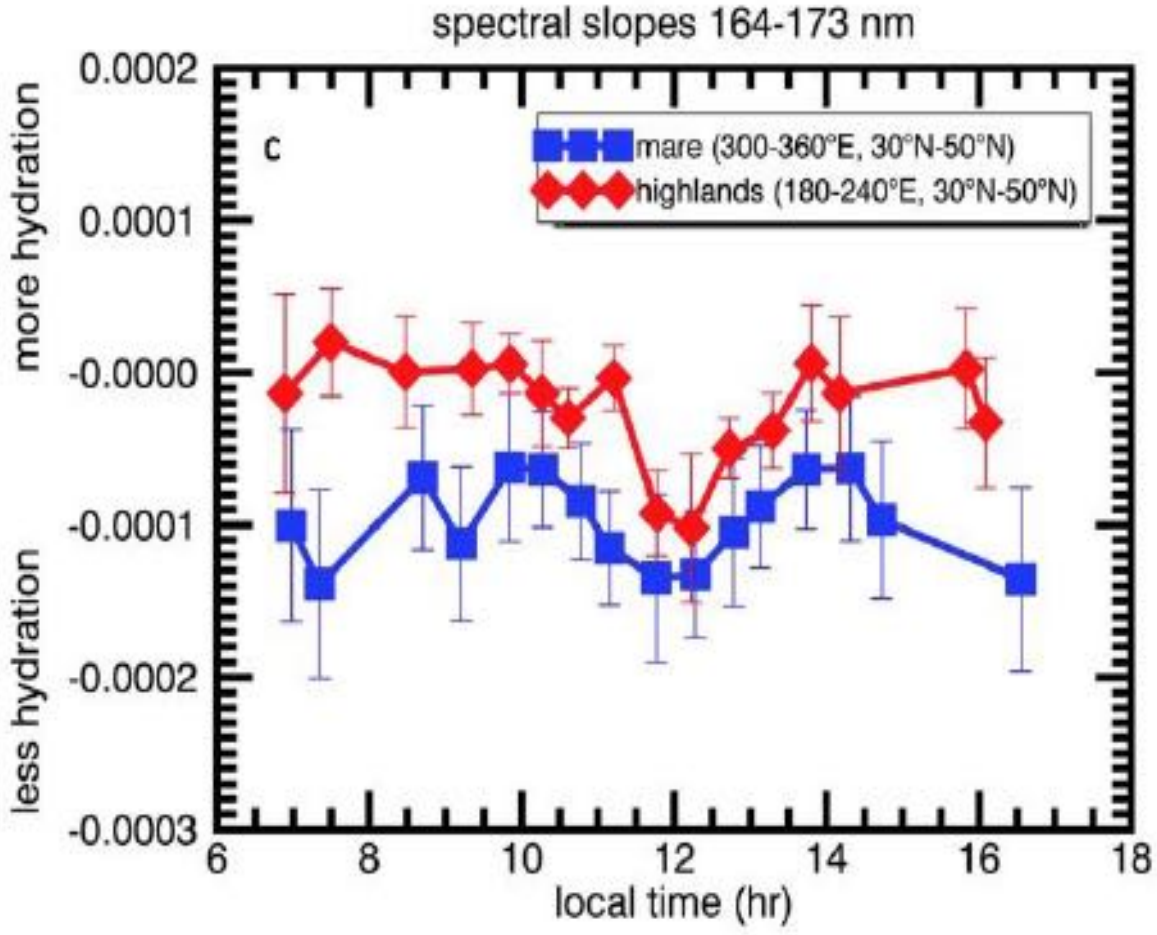
Three data sets from the M^3 on the Chandrayaan-1 space-craft, the VIMS on Cassini, and the extended mission for the Deep Impact Spacecraft collectively yielded evidence for the presence hydroxyl (and water ?) on the Moon.



A. M^3 data indicating the presence of a 3 μm band-edge feature typical of hydroxyl groups or possibly adsorbed water.
B. Simulation from Dyar and Hibbitts regarding the full band.

Migrating molecular water recently reported in LAMP measurements. *Hendrix, et. al, GRL, 46*(5), 2417- 2424 (2019).





Conclusions based on 1% of a monolayer and a > 1.2 eV binding energy.

Standard TPD: Data Analysis

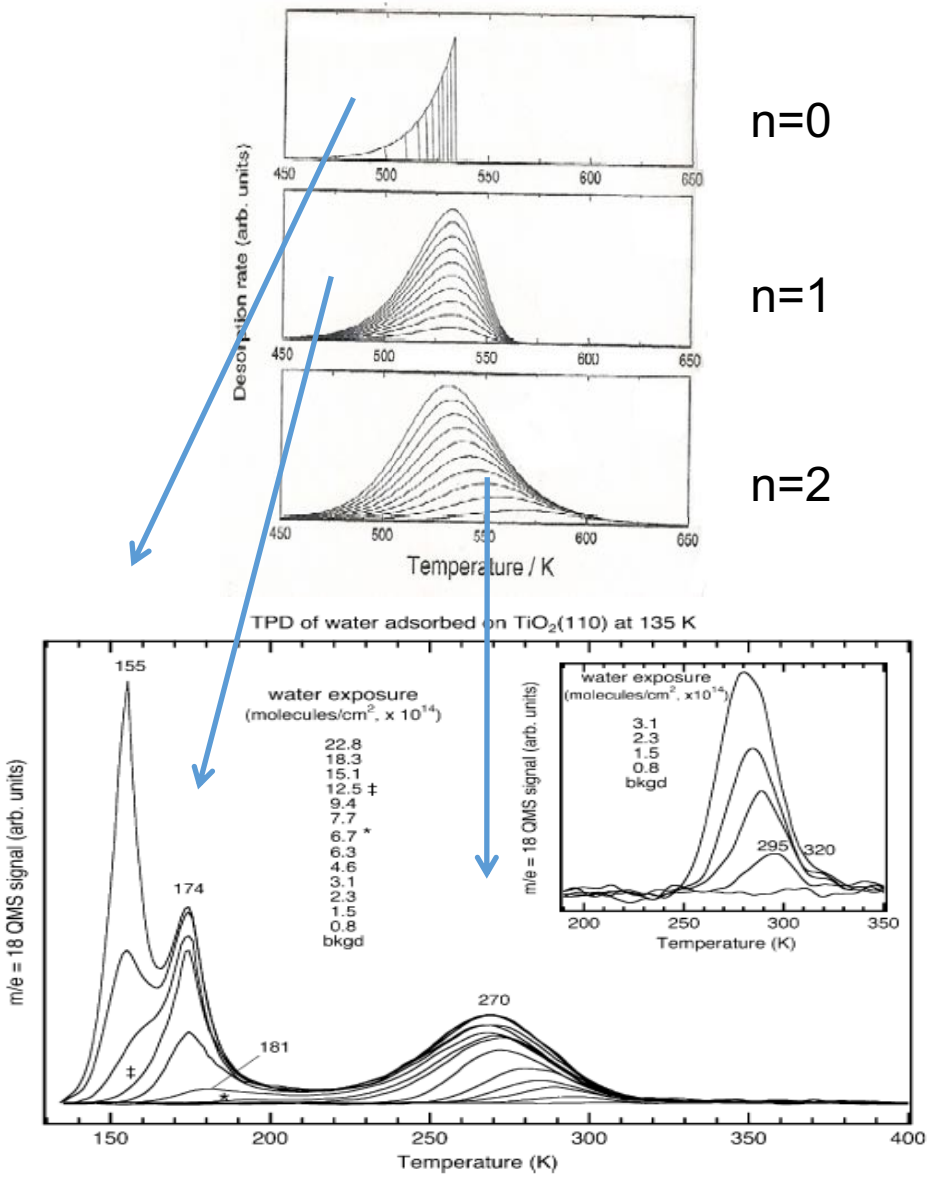
- Polanyi-Wigner equation

$$\theta' = -\nu \cdot \exp\left(-\frac{\Delta E_{des}}{RT(t)}\right) \cdot \theta^n$$

- θ the adsorbate coverage at time = t
- ΔE_{des} the energy of desorption
- T the temperature at time = t
- n the order of desorption
- The rate of desorption θ' is measured with the QMS

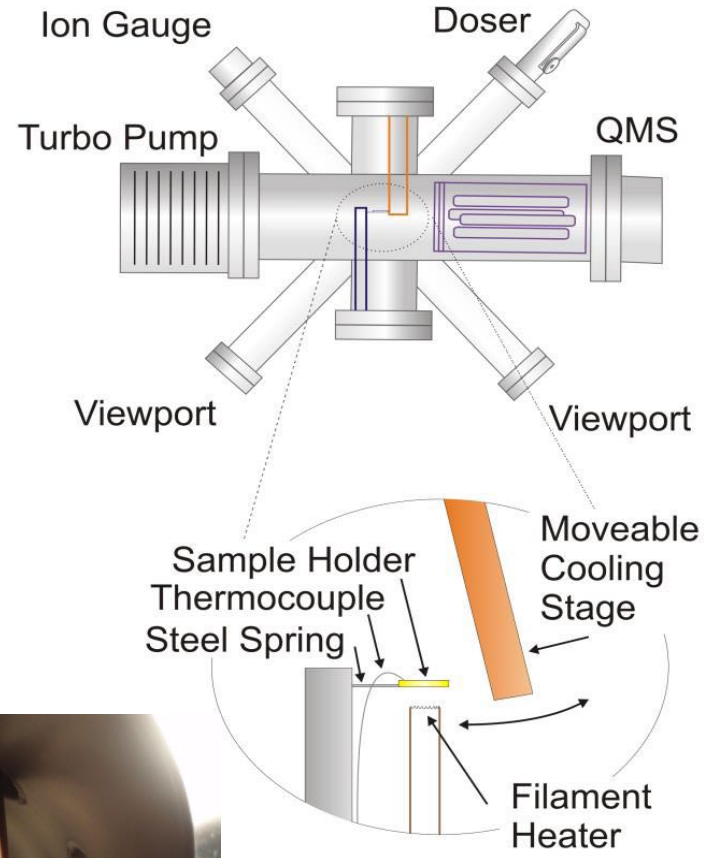
- Desorption energies are site-dependent

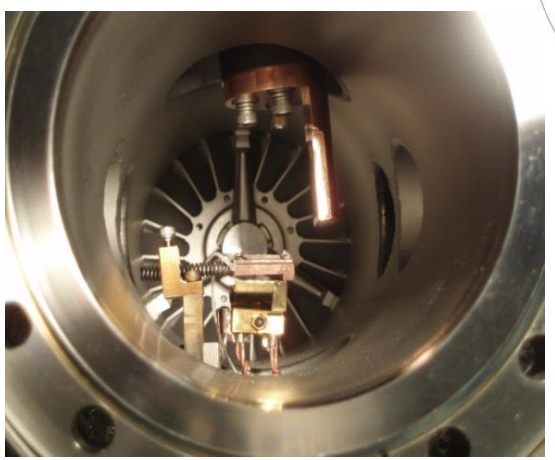
Physisorption < Molecular Chemisorption < Dissociative Chemisorption



"Novel" system for Temperature Programmed Desorption of mineral powders/regolith samples

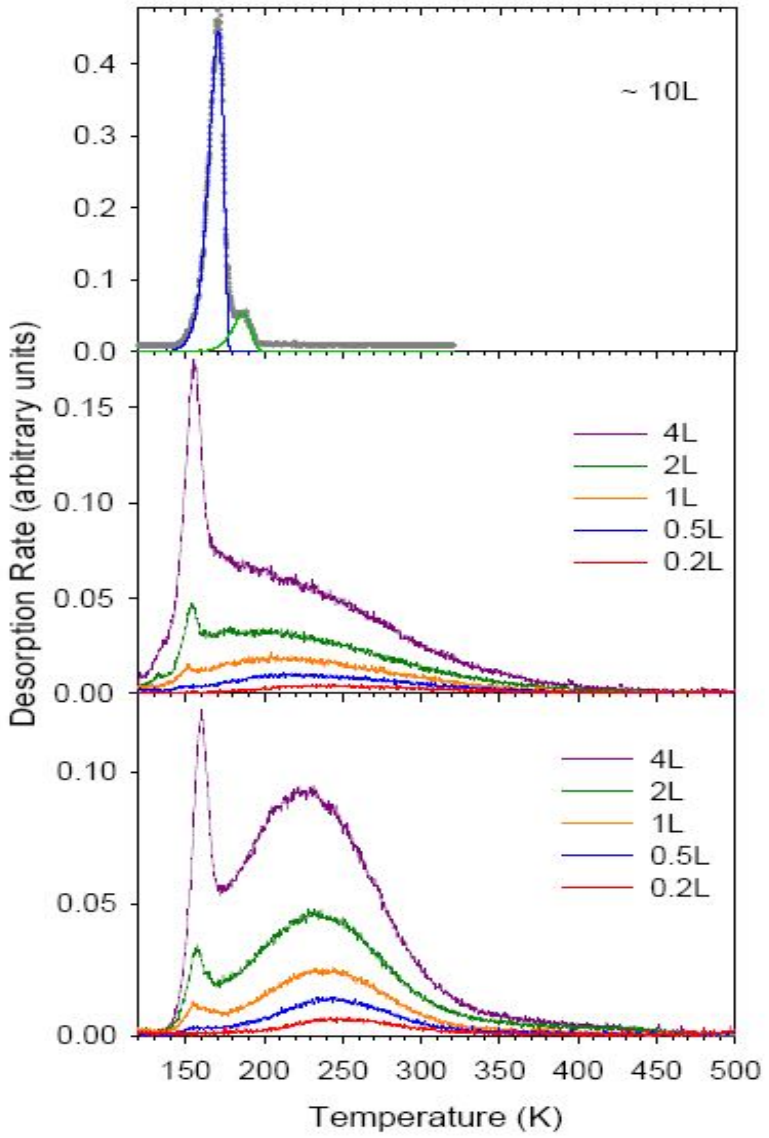
- The rate of release of an adsorbate is measured as a function of surface temperature – temperature programmed desorption (TPD).
- ***UHV < 2× 10^{-10} torr***
- Liquid Nitrogen cooling ***with detachable cooling connection***
- Effusive water dosing with calibrated ion gauge
- Dual filament heater (40W)
- QMS for detection of neutral desorbed species
- ***Gold-plated sample holder*** with type-K thermocouple
- <u>TPD of powders can be obtained WITHOUT background subtraction.</u>





Comparison of water TPD from three samples,

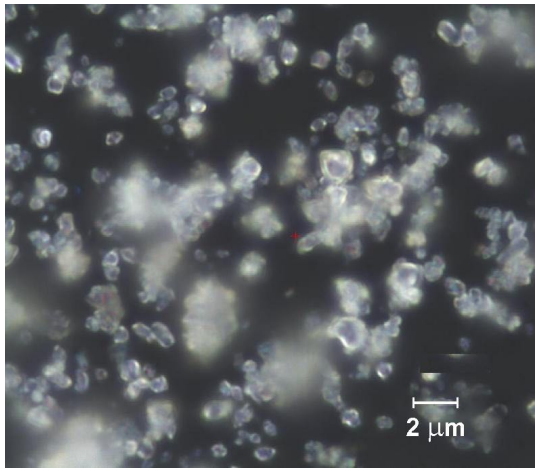
C. A. Hibbits, G. A. Greives, M. Poston, A. Alexandrov, M. D. Dyar, and T. M. Orlando, *Icarus* 213, 64 (2011).



K2294 glass, high iron, so more like the maria

JSC-1A, maria

surrogate



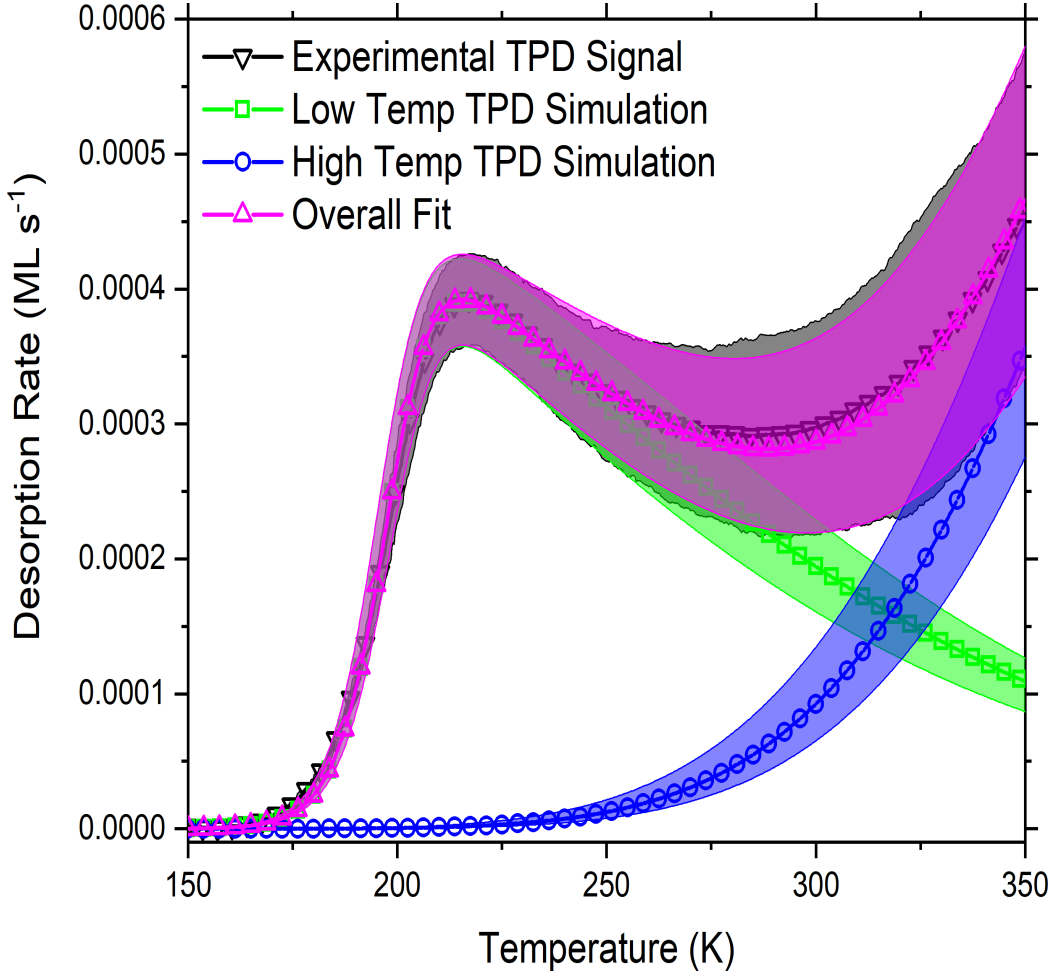
Albite, highlands surrogate – micronized

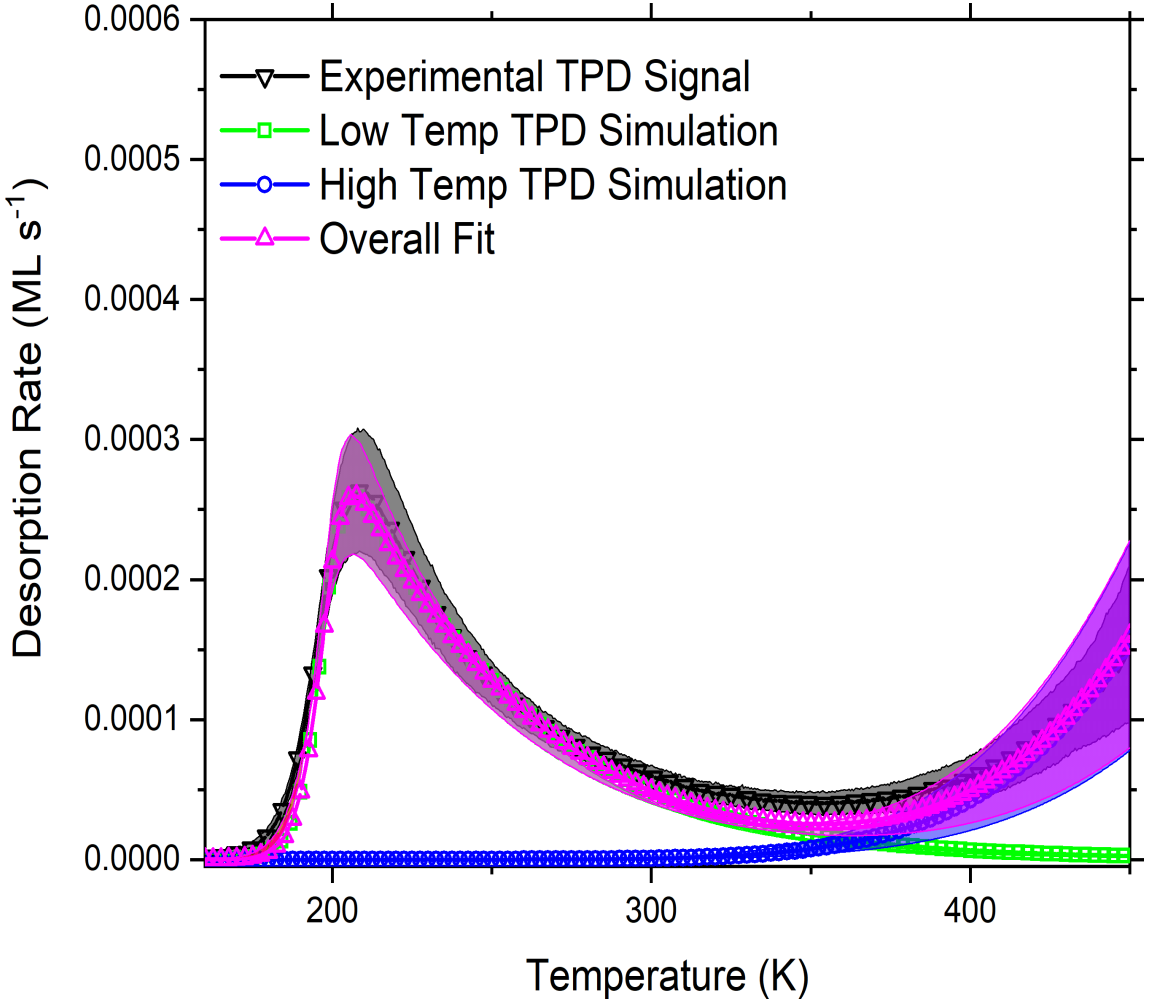
It is probably the surface defect/ grain boundary densities that matter with respect to binding water..

The more “glassy” the sample, the less is chemisorbs water. .

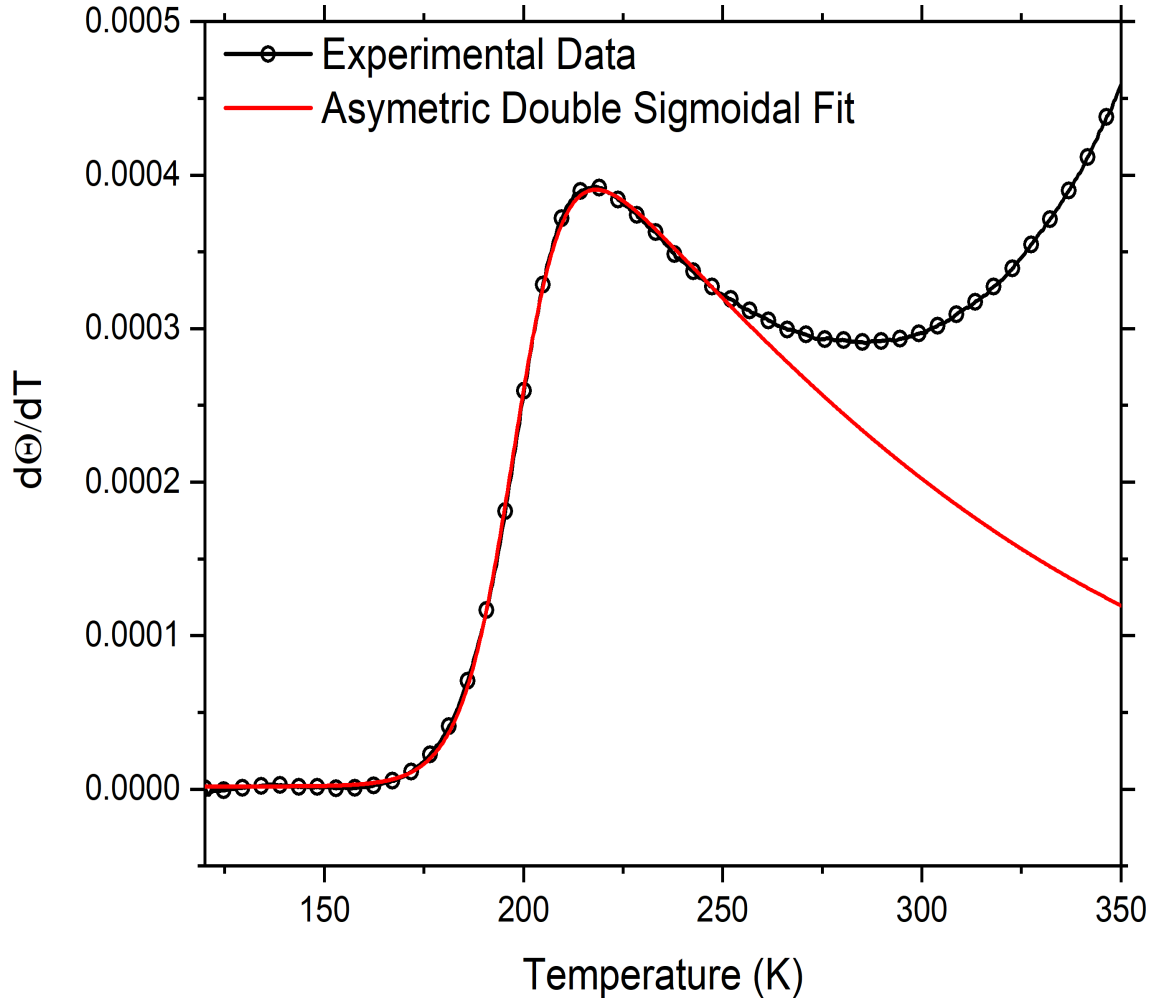
TPD of water from Apollo highland samples 14163 (left) and mare sample 10084 (right)

Samples dosed in vacuum with pure de-gased water at 180K -16 Langmuirs





TPD of Apollo 11 highland sample and peak fitting



An example of the asymmetric double sigmoidal fit to the experimental data.

The fit allowed extraction and separation of the low (red) and high temperature components (not shown).

Use the inversion method to extract coverage dependent activation energies from the low temperature feature.

Polayni-Wigner Equation :

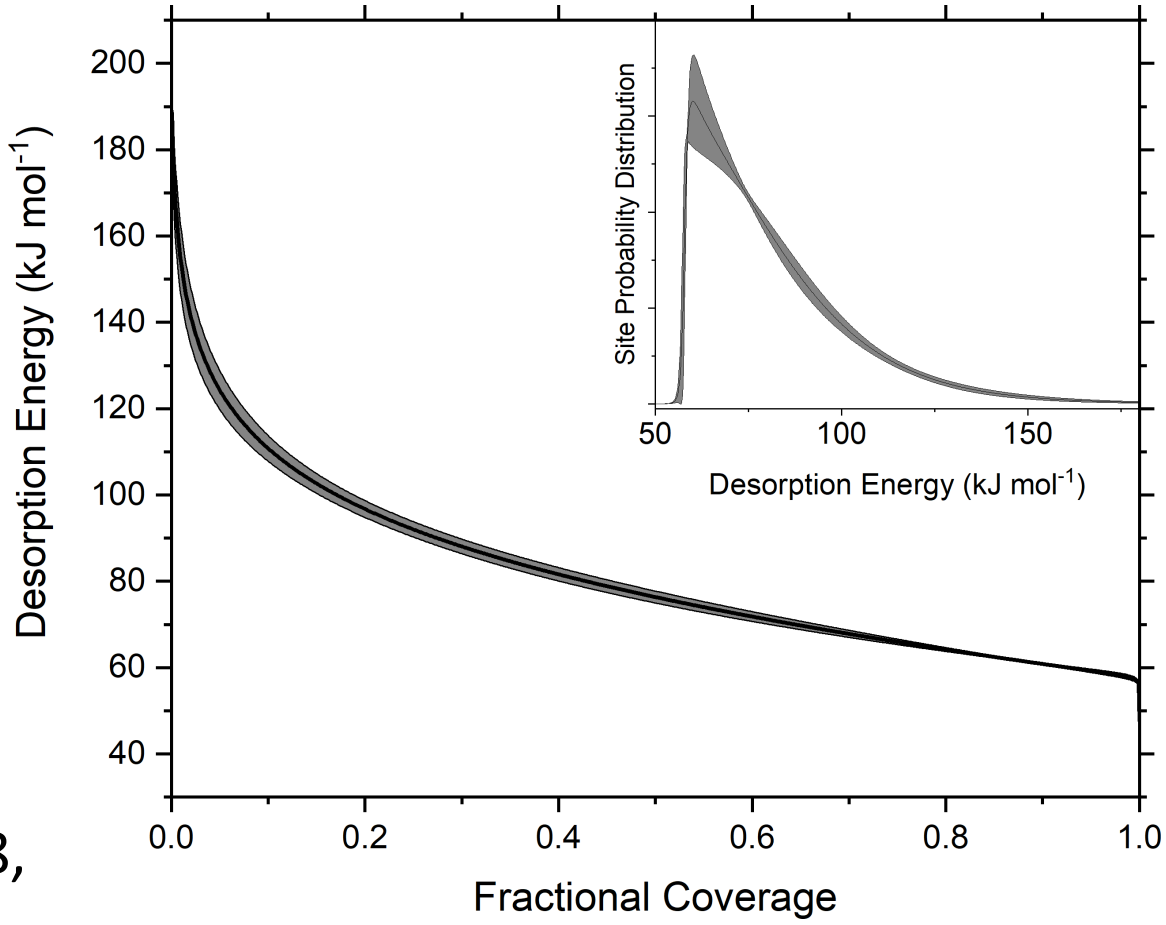
$$\frac{d\theta}{dt} = \nu\theta^n e^{\left(\frac{-Ea}{RT}\right)}$$

n is desorption/adsorption order

$E_{d,a}$ is desorption/adsorption energy

v is pre-factor or attempt frequency

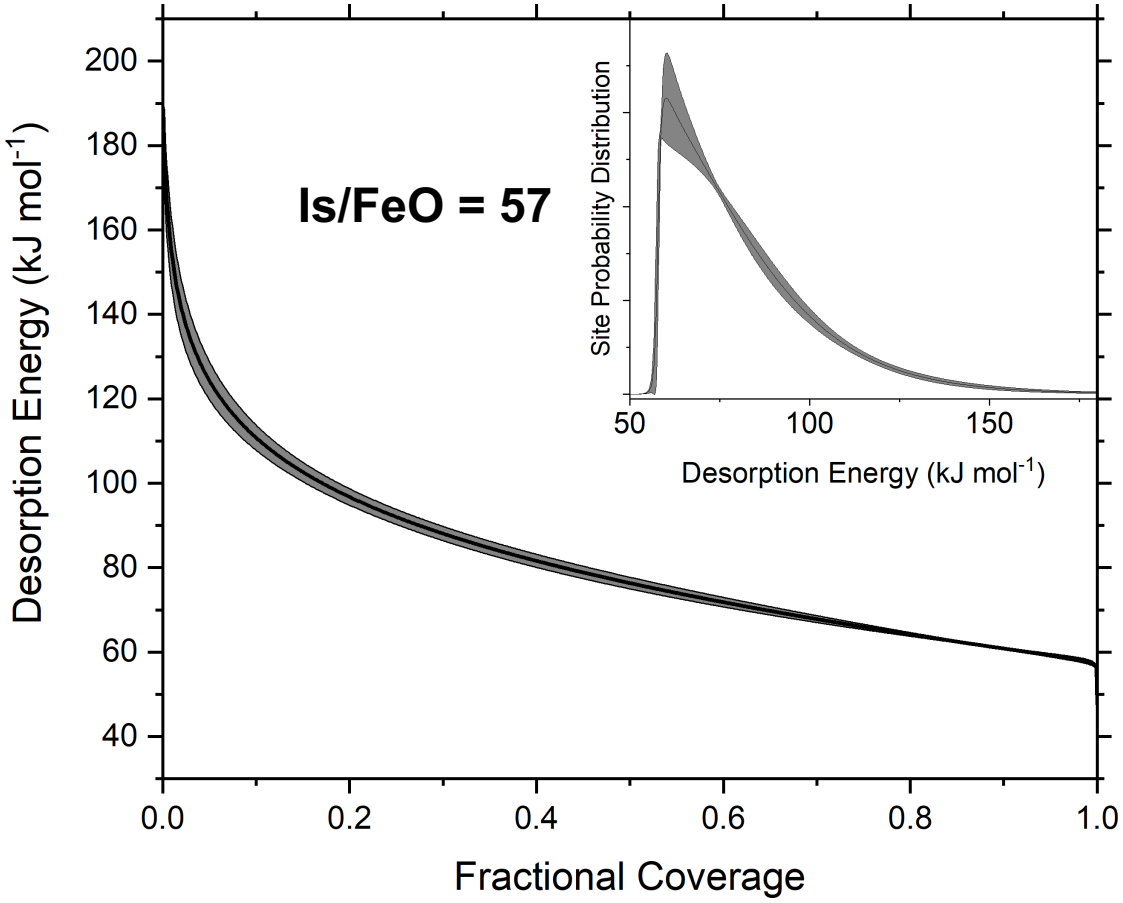
Solve for $E = -RTln\left(-\frac{d\theta/dt}{\nu\theta^n}\right)$

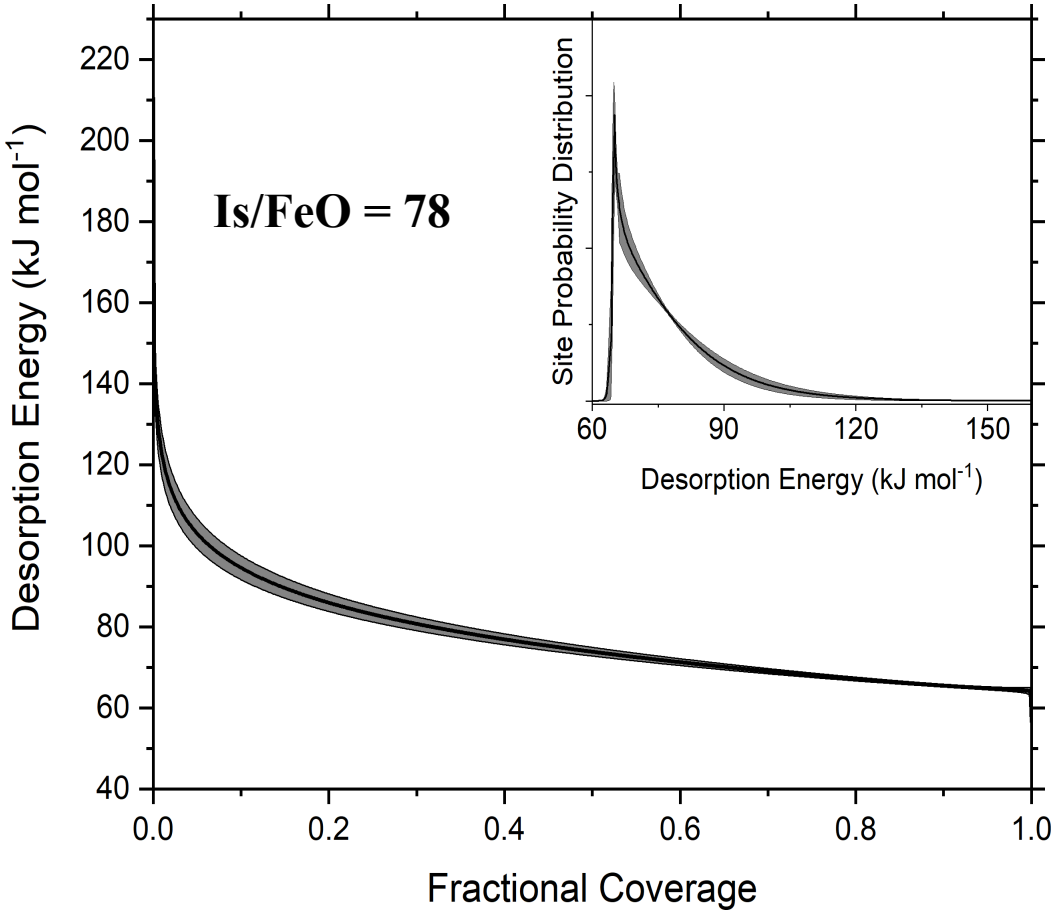


Tait, Steven L., et al. *J. Chem. Phys.* 164708, 2005

Highland vs. Mare distribution of activation energies.

Mare has narrower distribution and far less water. Likely due to “glass” or aggluntinate content (and possibly the relative amounts of Fe and Ti) Defects react to form terminal OH groups which nucleate ice and cluster formation



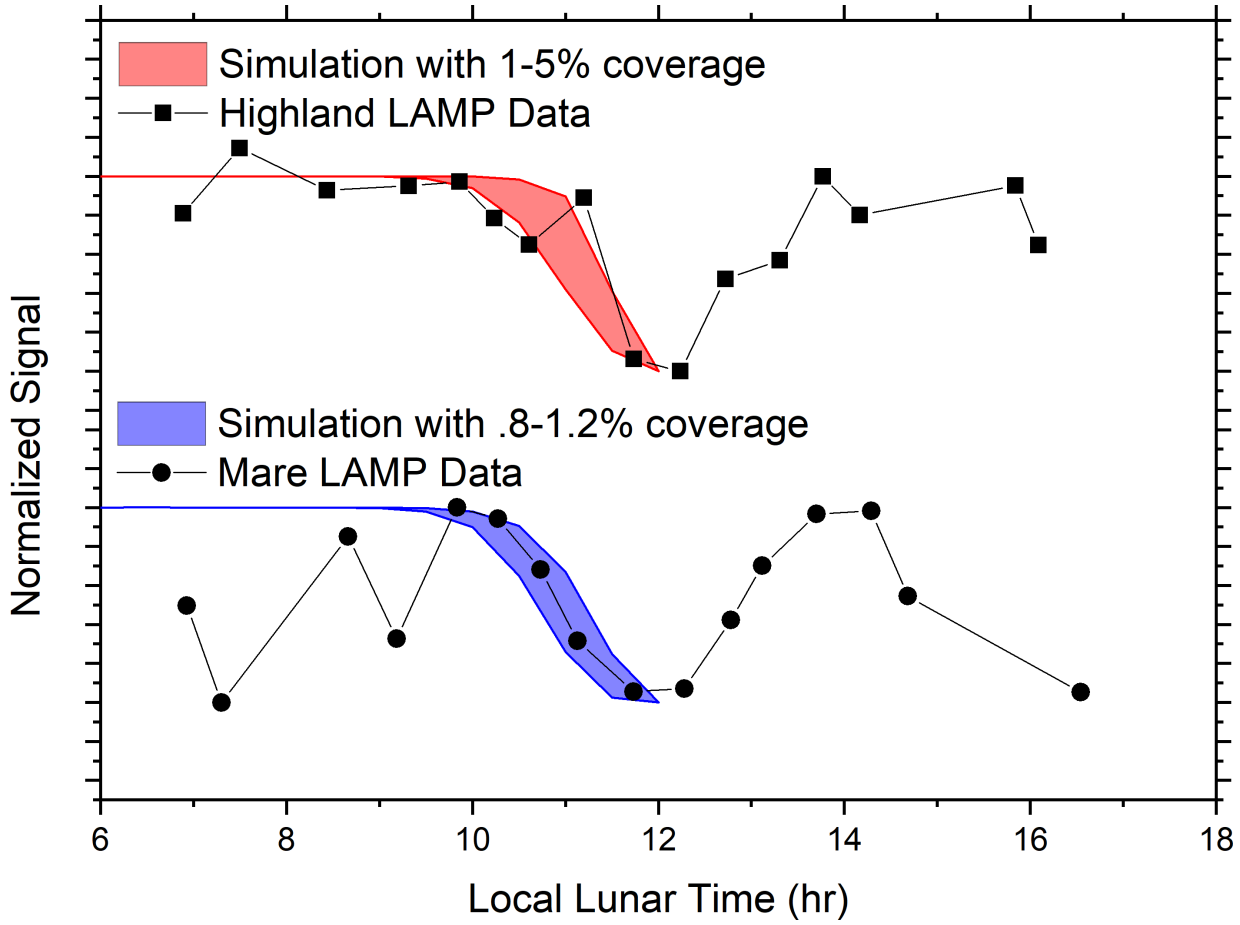


The extracted bonding energies used to simulate LAMP data. (1-5% Highland, .8-1.2%Mare)

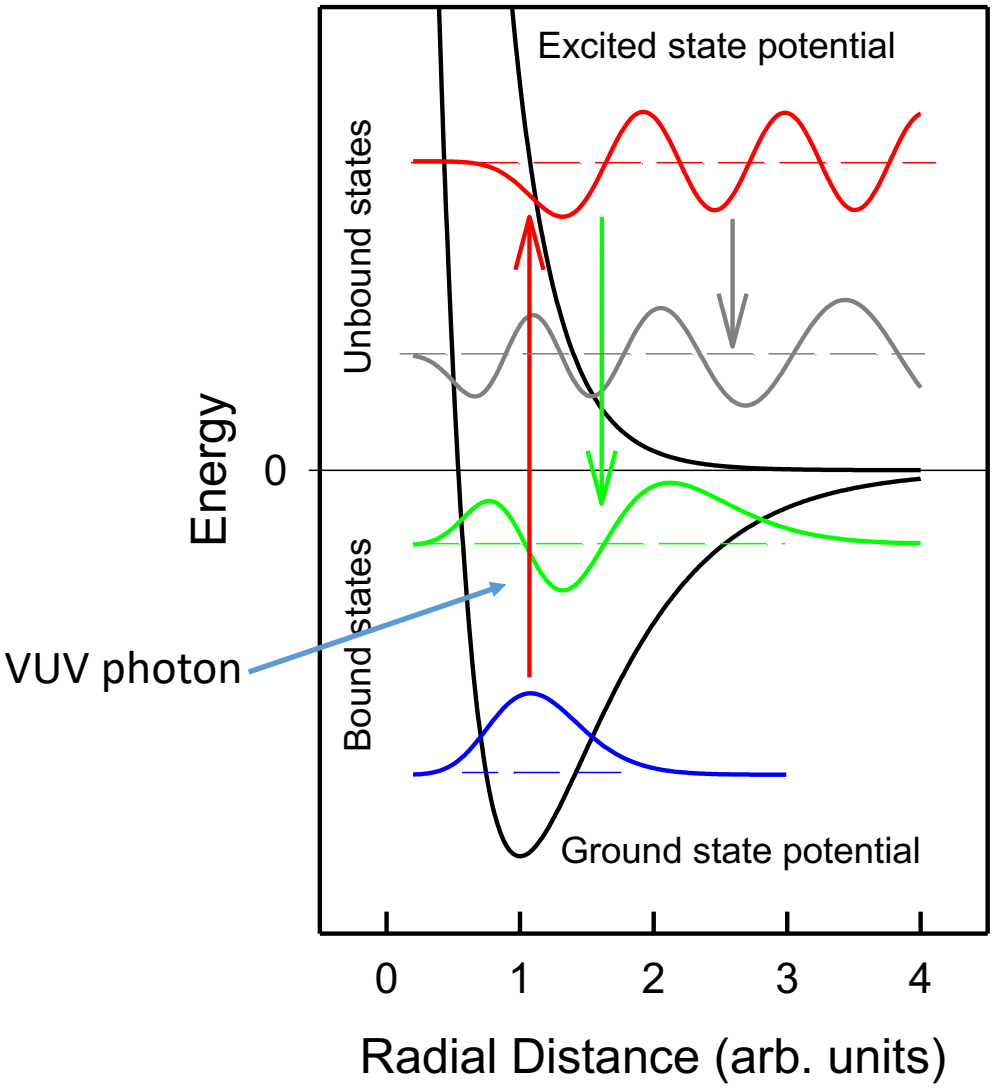
This works well but there is a twist….

Chemisorption is a SURFACE phenomena and VUV photons stimulate water removal effectively by photon-stimulated desorption and dissociation.

In addition to thermal desorption (TPD), we must consider PSD….i.e. the role of VUV photoabsorption.



Water VUV transition is NOT bound-to-bound. Photodesorption AND photodissociation happen



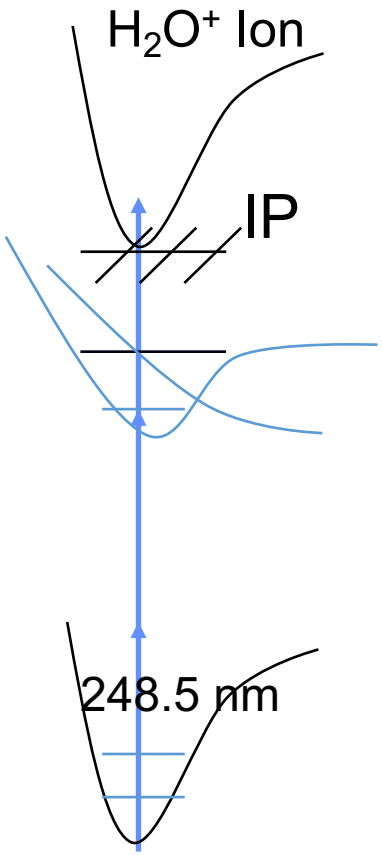
(1) An electronic excitation can excite the system from the ground state (water on regolith-blue) to an unbound state (red).

(2) The excited state wavefunction time-evolves in the unbound state and is water pushed away from the surface. Desorption

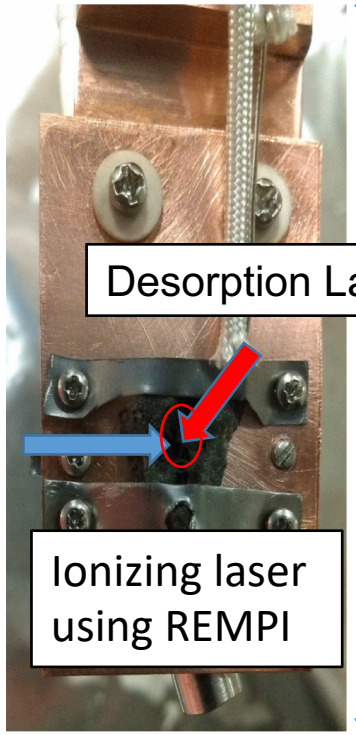
(3) If the energy exchanged from the regolith and charge density fills non-bonding levels on the water, the water dissociates.

(4) The total water REMOVAL rate is the sum of these.

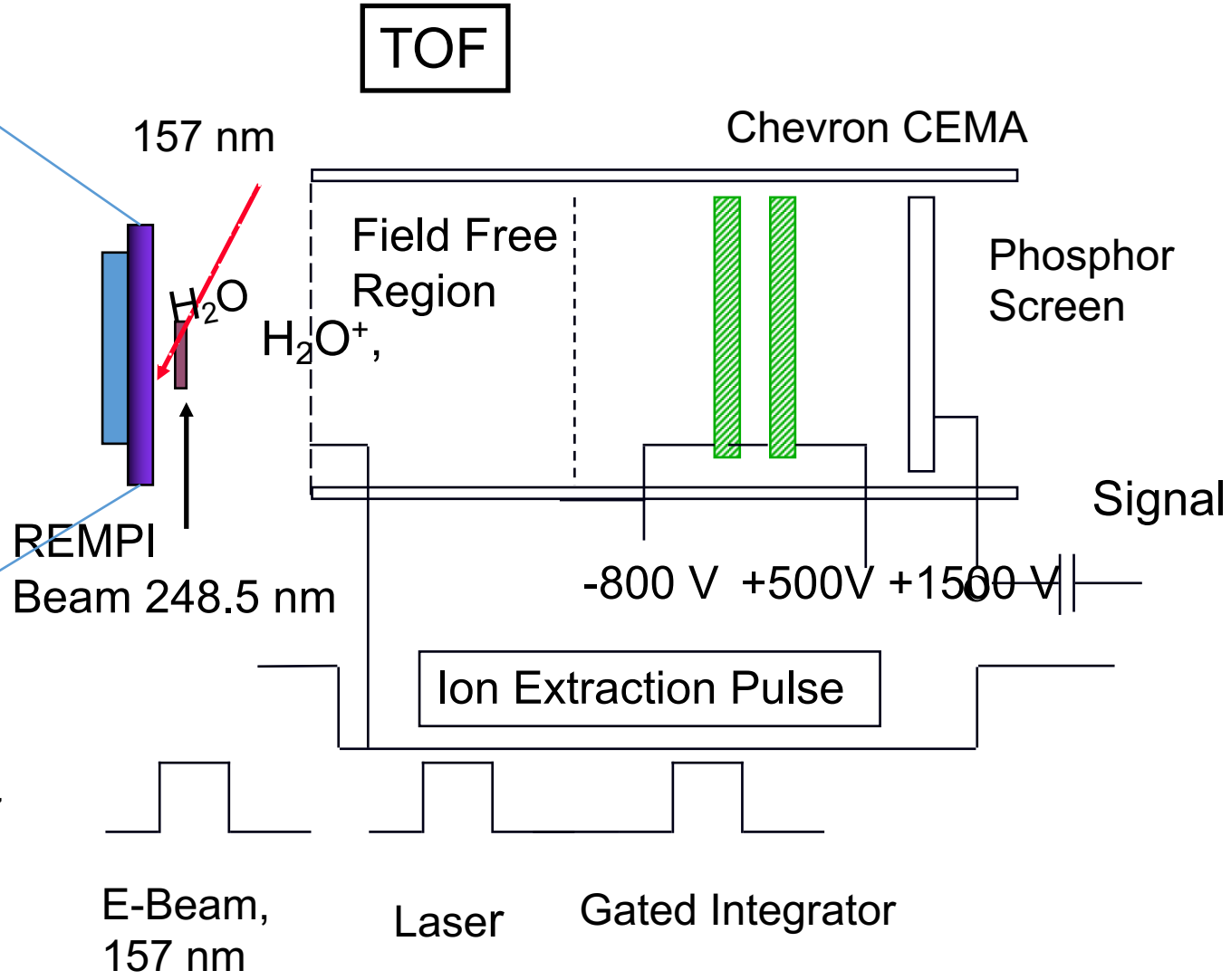
PSD or photodesorption: Laser Resonance Enhanced Multiphoton Ionization and ToF to detect desorbing wate



H_2O via 2+1 REMPI

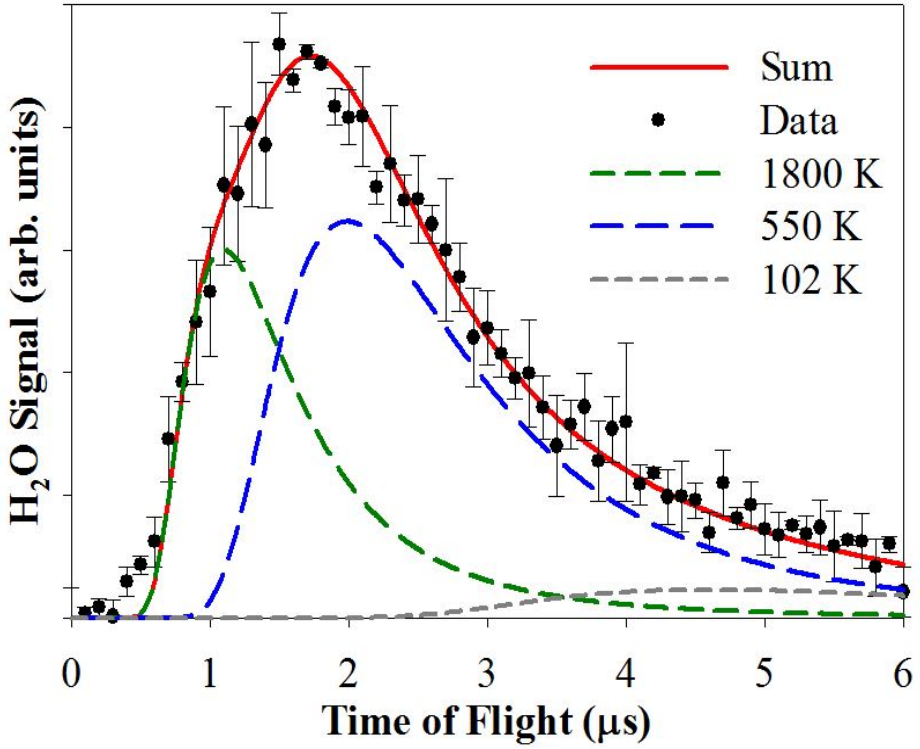


Impact Melt Breccia from Apollo 16 (pictured)
Mare Basalt from Apollo 17

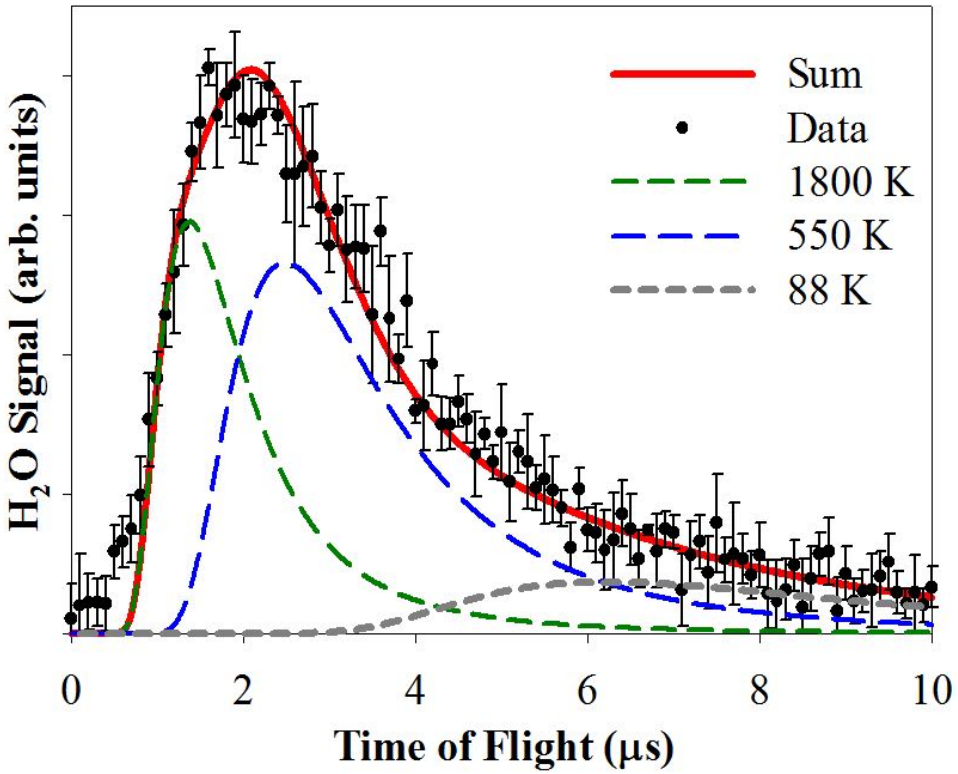


ToF spectra from lunar slabs-breccia and basalt

Breccia (r = 2.0 mm)



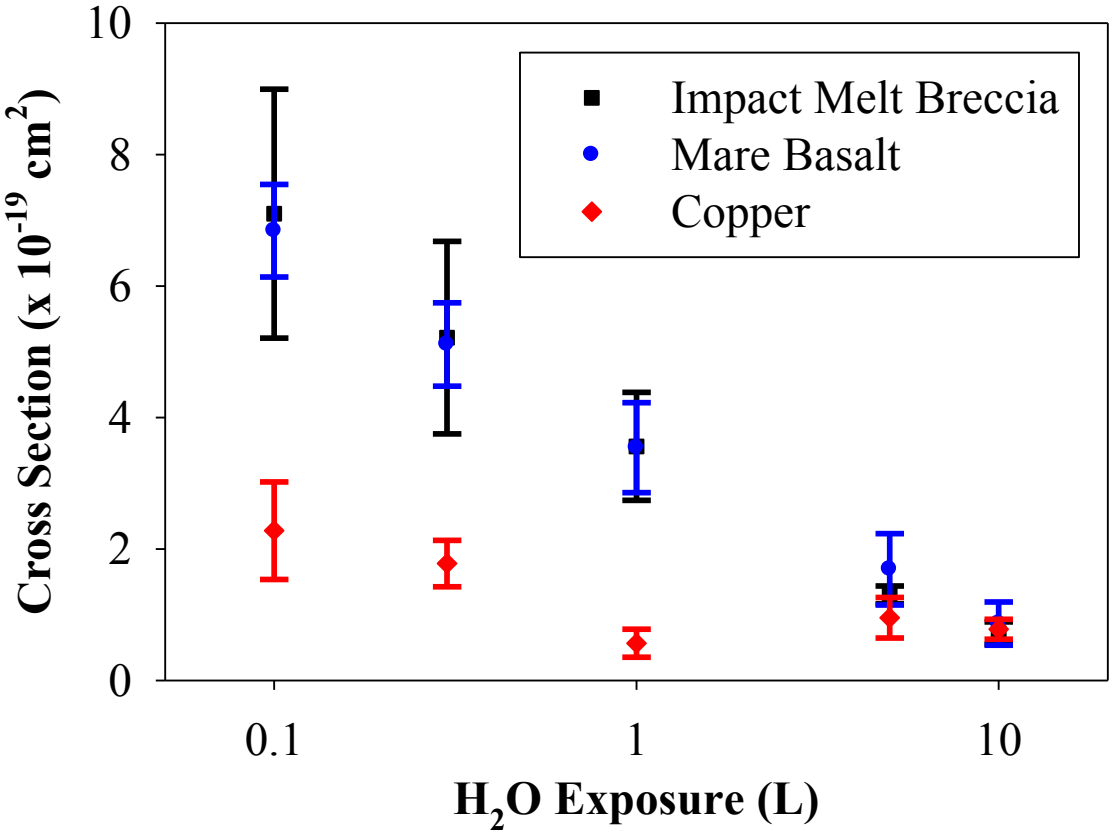
Basalt (r = 2.5 mm)



- 1 -20 L H_2O exposures yielded similar spectra shapes.
- Two non-thermal components may correspond to different adsorption geometries of water: oxygen down and oxygen up.
- Small thermal component was included.

First VUV absolute cross section for water photodesorption and photodissociation from an actual lunar sample

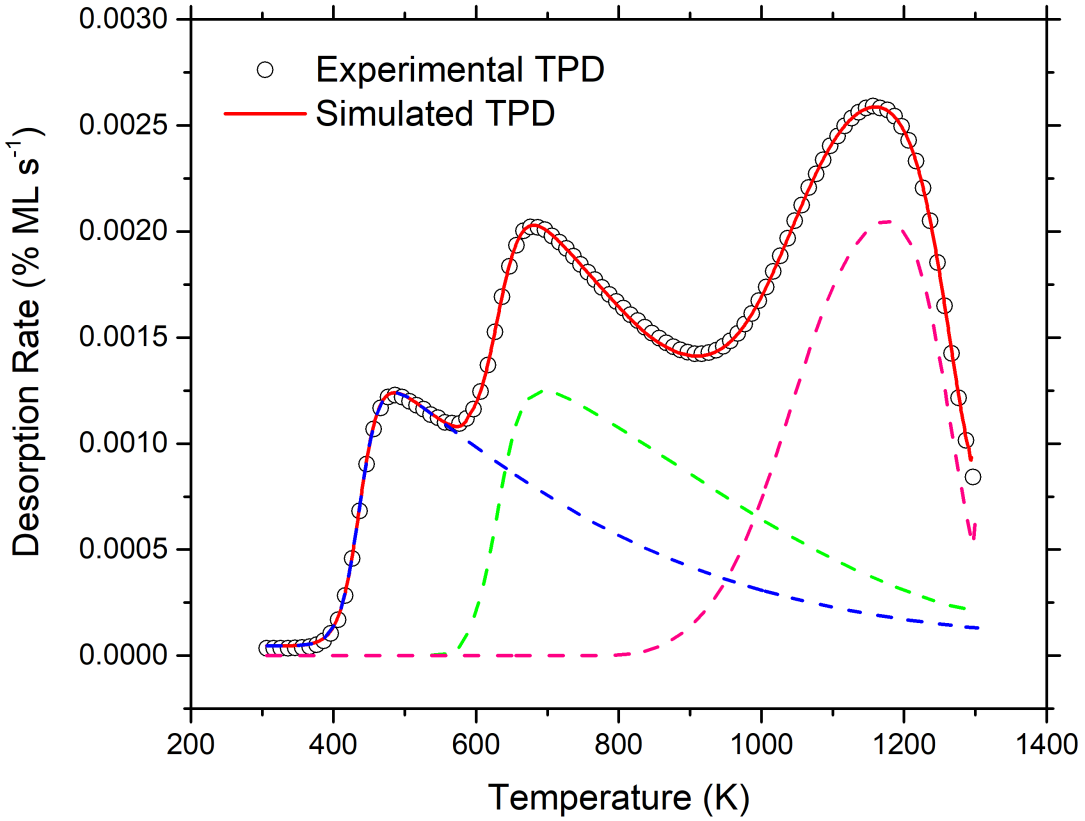
DeSimone & Orlando, JGR, doi:10.1002/2013JE004599
DeSimone & Orlando, JGR doi:10.1002/2013JE004598
DeSimone & Orlando, licarus.2014.08.023 (2014).

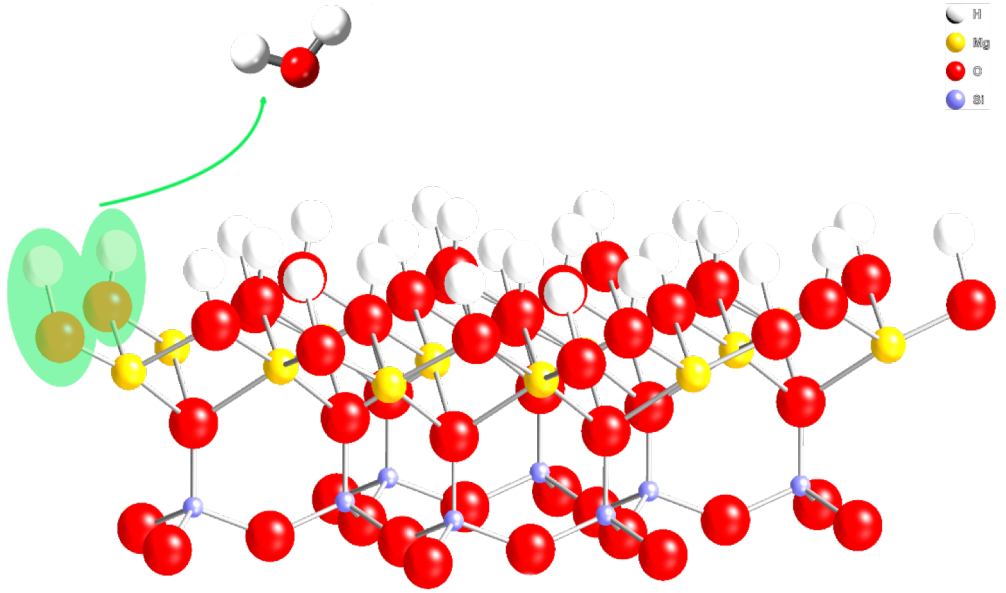


- The measured cross section yields a removal rate, $R_{H2O} = F_{ph}\ \sigma\theta$, of 40% of monolayer per diurnal cycle.
- PSD removal rate is high so if 1% of a monolayer remains there must be a source term that is greater than the removal rate.
- A possible source term is recombinative desorption.

LAMP results of 1% monolayer..... there appears to needs to be a diurnal source term.

Water PRODUCED and released from mare sample via recombinative desorption (RD). (Note: yield from highland is higher.)





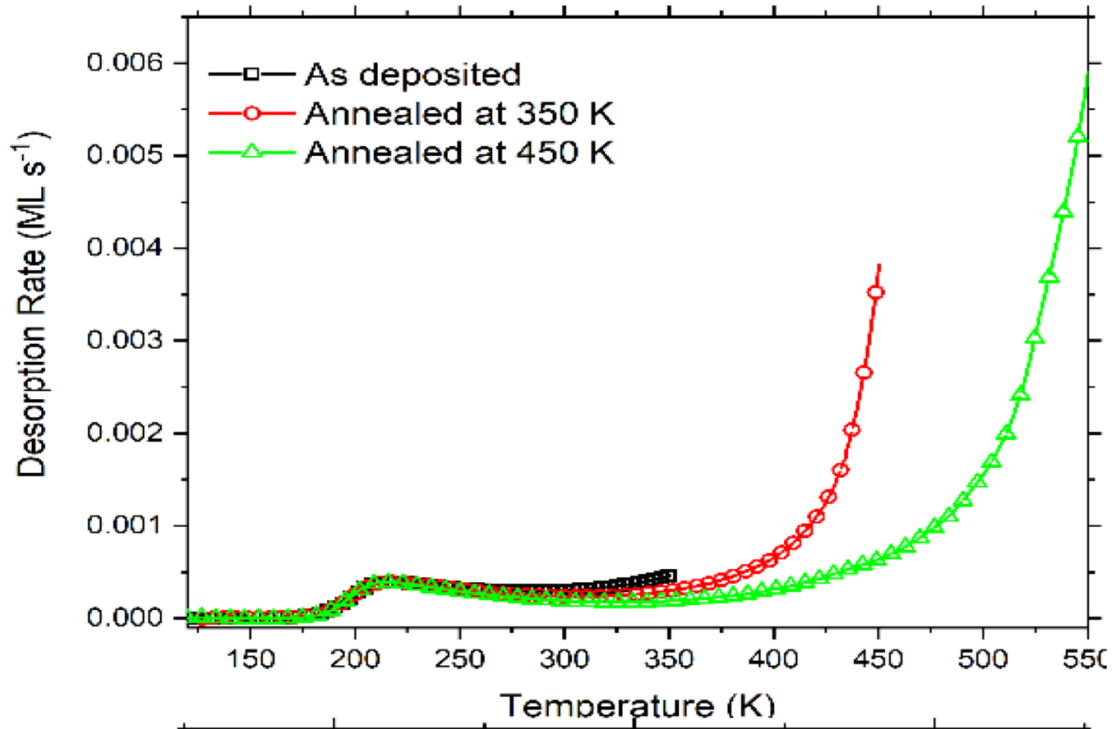
- ***<u>This implies that there may be more water (~ > 40% of a monolayer) migrating around grains nearly everywhere where T > 200K than we think.</u>***

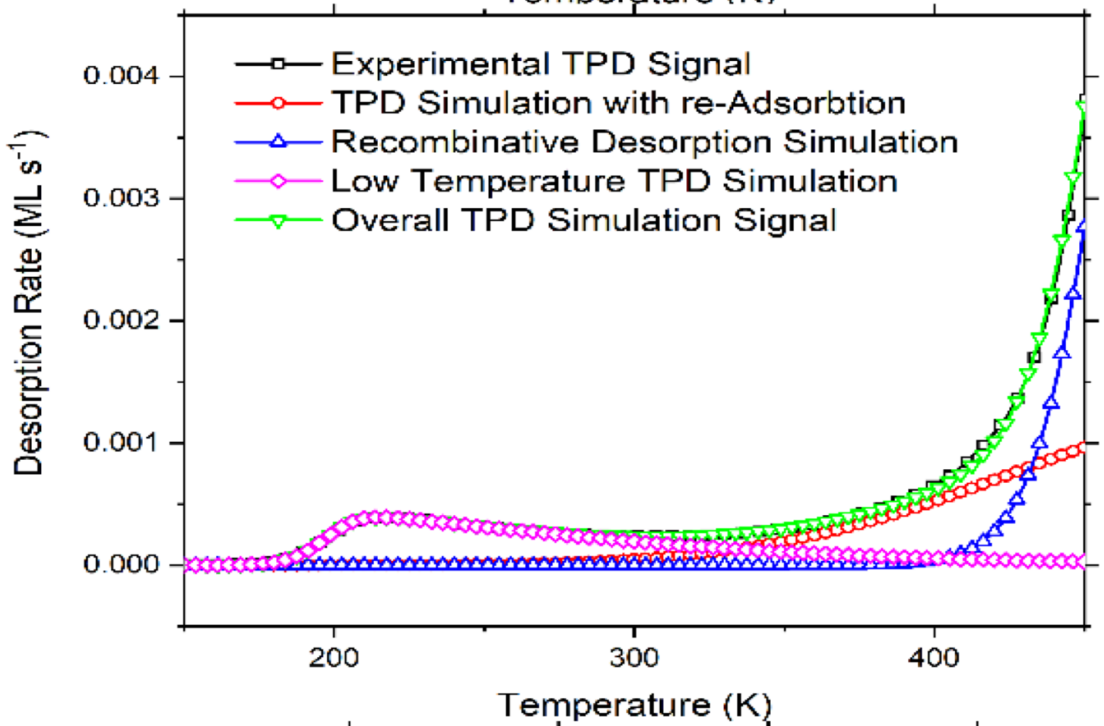
Some Conclusions…

- Water does not stick well to regolith. Binding energy on Mare and Highland samples typically ~ 0.6 eV but with some sites up to 1.2 eV.

- LAMP data can be modeled with high binding energy state. However, PSD (non-thermal desorption) has a high cross section for water removal and dissociation.

- Water can be produced by a process known as recombinative desorption. Activation energy is ~ 0.8 eV and is most important for materials with Fe, Ti and Mg oxides. This could be a diurnal source of water needed to explain the equilibrium concentration observed by LAMP.


As deposited
Annealed at 350 K
Annealed at 450 K
Desorption Rate (ML s-1)
0.006
0.005
0.004
0.003
0.002
0.001
0.000
150
200
250
300
350
400
450
500
Temperature (K)


Experimental TPD Signal
TPD Simulation with re-Adsorbtion
Recombinative Desorption Simulation
Low Temperature TPD Simulation
Overall TPD Simulation Signal
Desorption Rate (ML s-1)
0.004
0.003
0.002
0.001
0.000
200
300
400
Temperature (K)